

Features of aluminum anodic behavior in media with various pH values in the presence of sodium chloride and glycine

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Abstract

The anodic behavior of aluminum in aqueous solutions with various concentrations of NaCl and glycine (pH = 4.8–8.5) was studied. It has been shown that the metal is in a passive state in the presence of glycine zwitter-ions (pH = 4.8–5.8), but local destruction of the metal surface occurs in the presence of Cl[−] and Gly[−] ions. A possible reason for the observed effect of glycine zwitter-ions may lie in the strong intermolecular hydrogen bonds that are formed between the amino and carboxy groups and prevail over the interaction of these groups with the oxidized aluminum surface. The corrosive action of Cl[−] and Gly[−] ions against aluminum that causes its local activation at all the studied concentrations (from $1.3 \cdot 10^{-4}$ M to $1.7 \cdot 10^{-1}$ M) of NaCl (pH = 4.8–5.8) and glycine (pH = 8.5) has been proved. The type of corrosion products differ essentially depending on the pH, concentration and thermal conditions. The experimental results that we obtained are interpreted within the framework of modern competitive adsorption, complexing and nucleophilic substitution theories. They have been confirmed by independent physical and chemical methods (electrochemical and scanning electron microscopy combined with X-ray spectral microanalysis). In the presence of chloride ions, the pit formation process is a nucleophilic substitution reaction of associative type, whereas in the presence of glycine anions, it is of dissociative type.

Keywords: *aluminum, sodium chloride, pH, glycine, local activation.*

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Introduction

The question of the effect of anion nature on the local destruction of oxidized aluminum surface still attracts the attention of researchers due to the complexity of its mechanism and the need to take into account the composition of surface films that have not been studied in sufficient detail. A progressive step in the analysis of this issue was made by in the works by G.V. Akimov who was among the first to express and justify the assumption about corrosion process mechanism on aluminum in the presence of chloride ions, both during self-dissolution and during anodic polarization [1]. The present article attempts to solve this problem based on systematic studies of the aluminum anodic behavior in a series of solutions containing not only inorganic (sodium chloride) but also of organic compounds (glycine) that are widely used in modern applied electrochemistry and corrosion science to identify the general and specific patterns of processes occurring in these solutions.

Experimental

This study was performed on a stationary aluminum electrode (99.9%). Before each experiment, the metal surface was machined (sanded on sandpaper with a decreasing grain radius, followed by polishing on filter paper) and washed with distilled water.

NaCl solutions with nearly neutral pH (concentration range $1.7 \cdot 10^{-4}$ to $1.7 \cdot 10^{-1}$ M; pH=4.8–5.6), as well as aqueous (pH=4.8–5.6) and slightly alkaline (pH=8.5) media with addition of glycine (concentration range $1.3 \cdot 10^{-4}$ to $1.3 \cdot 10^{-1}$ M) prepared from reagents of “pure for analysis” and “chemically pure” grade on distilled water were used as working electrolytes. The pH of the working electrolyte was measured in each experiment using an N 5123 pH-meter (accuracy ± 0.1). The experiments were carried out in a three-electrode electrolytic cell with divided cathodic and anodic spaces under naturally aerated conditions. A silver chloride reference electrode ($E = +0.20$ V) was used. All the potentials in this work were converted to the normal hydrogen electrode (NHE) scale. A platinum counter electrode was used.

To obtain reliable results, a complex of independent physicochemical methods (electrochemical and microscopic methods, X-ray spectral microanalysis, pH-metry) was used.

Electrochemical experiments were carried out at a temperature of $20 \pm 2^\circ\text{C}$ using an IRC-Compact potentiostat with a FRA frequency analyzer and Equivalent Circuits Solver software (Ver 1.2). Two types of measurements were performed by recording voltammetric and chronoamperometric curves, which were used later to estimate the quantitative characteristics of pit formation (PF) on aluminum. The primary stage of the experiment involved the recording of voltammetric curves according to following procedure. After immersing the electrode in the working electrolyte and exposing it for 10 minutes, a potentiodynamic anodic voltammogram was recorded at a potential scanning rate of $v = 0.2$ V/min in the region of positive values. A sharp increase in the anodic current on the voltammogram allows one to determine the PF potential (E_{PF}), *i.e.*, – a critical value of the potential, which is the local activation potential (E_{LA}).

However, it is necessary to distinguish the E_{PF} , at which pitting is stable, from the local activation (LA) potential that characterizes the initial stage of the PF, *i.e.*, the occurrence of the very first metastable pitting. In order to understand the mechanism of metal depassivation, it is the LA potential (E_{LA}) that is of paramount importance in the theory and practice of inhibitory protection [2].

The E_{LA} potential was determined by chronoamperometry. In order to obtain the chronoamperograms, the primary treatment of the electrode was carried out by the method described above, after which the sample was polarized anodically at different potentials near the LA potential, and the variation in current over time was recorded. In this case, the shape of the $i = f(\tau)$ plots that we obtained is a criterion of the type of destruction of the electrode surface [3]: an exponential decrease in the anodic current characterizes a passive state of the metal, a growth indicates the surface activation, and fluctuations are typical of LA. According to the analysis of the chronoamperograms, the main quantitative characteristics

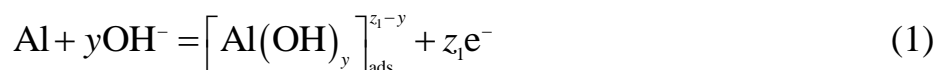
of the metal PF process were determined [3]: the LA potential (E_{LA}), the resistance to LA ($\Delta E_{LA} = E_{LA} - E_{COR}$), the PF induction period (τ_{ind}), and the rate of the LA process (a value proportional to $1/\tau_{ind}$).

Electrochemical studies were supplemented by the visual examination of the working electrode surface before and after each experiment (anodic polarization or chronoamperometric measurements) on MBS-2 ($\times 7$) and MIM-7 ($\times 500$) optical microscopes. The degree of metal damage in the solutions studied was determined from the surface topography. In addition to the visual control of the working electrode surface, qualitative and quantitative chemical analysis of the products formed on it after an experiment was carried out by scanning electron microscopy combined with X-ray spectral microanalysis using an energy-dispersive X-ray INCA Energy-250 attachment (Oxford Instruments) to JEOL 6380LV scanning electron microscope (SEM/RSMA) [4, 5].

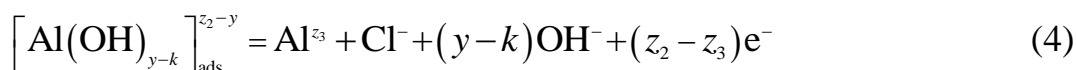
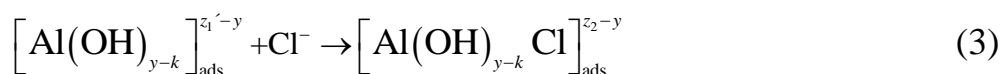
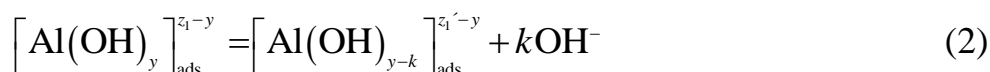
Results and discussion

The PF of aluminum surface under anodic polarization conditions in chloride-containing media was detected by electrochemical (Figure 1) and microscopic (Table 1) methods in the studied range of NaCl concentrations. As noted above, a great contribution to the study of the mechanism of the activating action of chlorides was made by G.V. Akimov, who associated it back in 1951 with the destruction of the oxide passivating film due to adsorption of chloride ions on the surface that displace oxygen when a certain potential is reached [1]. Without denying this concept, the results obtained in the present study were interpreted using the theory of “hard and soft acids and bases” (HSAB theory) and the nucleophilic substitution model [2, 6, 7]. This complicates the general scheme of the aluminum PF mechanism that includes the following stages:

- formation of a passivating film on the metal surface:



- PF process:



In the last stage, the reaction of the passive metal with the corrosive solution components results in adsorbed surface complexes $\left[\text{Al}(\text{OH})_{y-k} \text{Cl} \right]_{\text{ads}}^{z_2 - y}$ (probably aluminum dihydroxychloride $\text{Al}(\text{OH})_2\text{Cl}$). An indirect confirmation that such complexes exist on the surface of aluminum is that the Cl element is detected on it by the RSMA method (Table 2). However, according to the HSAB concept, this compound is stable because it is generated

by a hard acid and a hard base (according to the Pearson principle: Al^{3+} , AlCl_3 , and Al_2O_3 are hard acids, whereas OH^- and Cl^- are hard bases) [2]. Subsequently, the soluble complexes formed on aluminum surface are transferred to the electrolyte bulk, which facilitates the PF process.

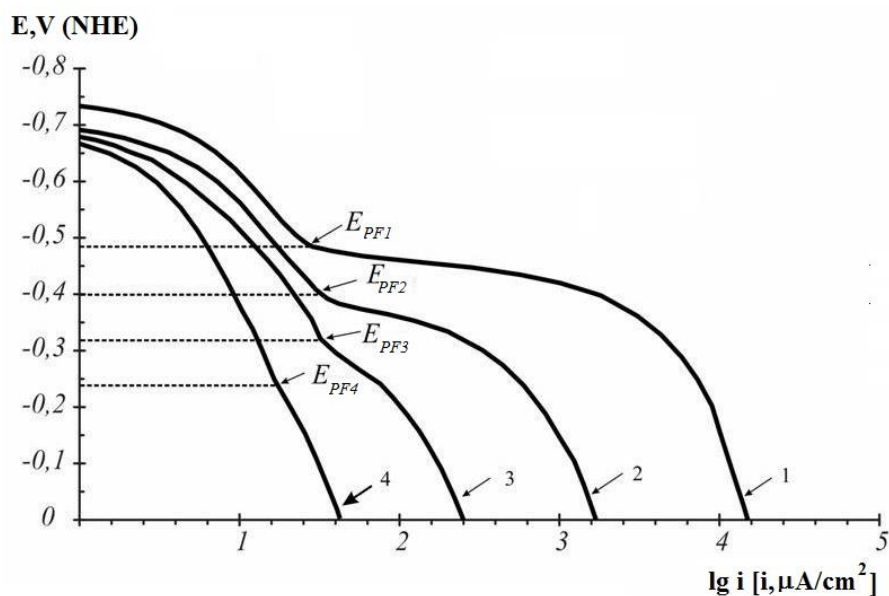


Figure 1. Anodic polarization curves (APC) of aluminum in $1.7 \cdot 10^{-4}$ M (1), $1.7 \cdot 10^{-3}$ M (2), $1.7 \cdot 10^{-2}$ M (3) and $1.7 \cdot 10^{-1}$ M (4) NaCl solutions ($v = 0.2$ V/min, $t = 20^\circ\text{C}$).

Table 1. Micrographs of aluminum surface after APC recording in the solutions studied (the \rightarrow arrow indicates local corrosion).

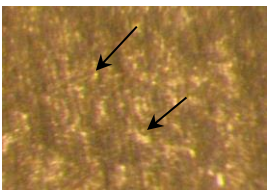

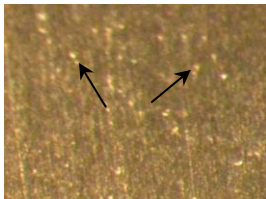
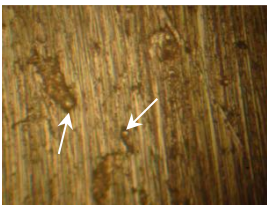

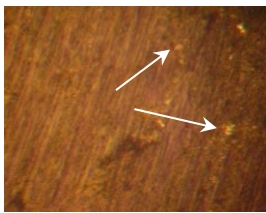

	NaCl, $1.7 \cdot 10^{-1}$ M (pH 5.6)	Gly, $1.3 \cdot 10^{-1}$ M (pH 5.8)	Gly, $1.3 \cdot 10^{-1}$ M (pH 8.5)
MBS-2 ($\times 7$)			
MIM-7 ($\times 500$)			
Pit depth	$\sim 12 \mu\text{m}$	—	$\sim 6 \mu\text{m}$

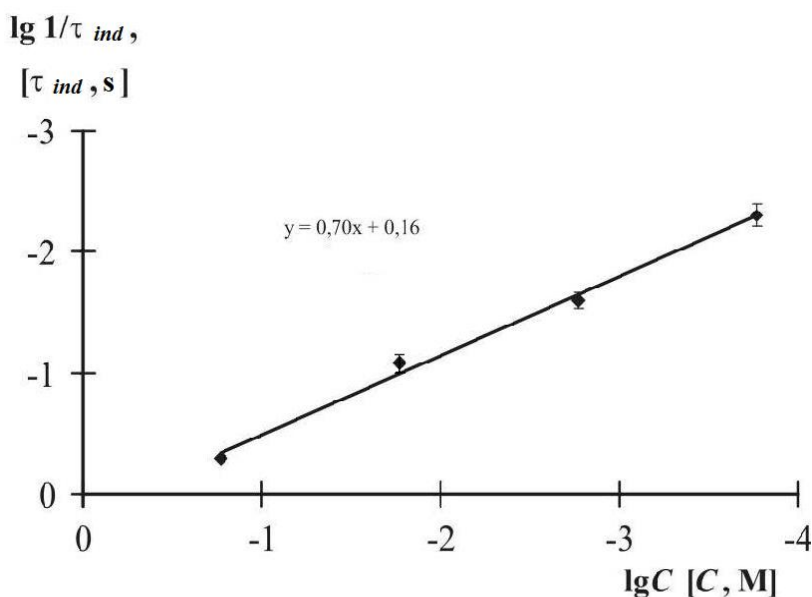
Table 2. RSMA of aluminum surface (in the selected zones) after voltammetric studies in $1.7 \cdot 10^{-1}$ M NaCl solution at 20°C.

	RSMA		Surface micrograph (SEM, ×1000)
	Element	Weight %	
NaCl $1.7 \cdot 10^{-1}$ M	Al	38.06	
	O	47.47	
	Cl	11.59	
	Na	1.89	
	Si	0.99	

To specify the limiting stage of the aluminum PF mechanism described above, the $\lg 1/t_{\text{ind}}$ vs. $d\lg C_{\text{Cl}^-}$ plot was built (Figure 2). Based on the provisions of formal kinetics: $1/t_{\text{ind}} = kC_{\text{Cl}^-}^n$ [6, 7].

Therefore, $n_{\text{Cl}^-} = d(\lg 1/t_{\text{ind}})/d\lg C_{\text{Cl}^-} = 0.7 \rightarrow 1$.

The data obtained allow one to assume that the limiting stage of the PF process presented above is stage (3), *i.e.*, association of the $\left[\text{Al}(\text{OH})_{y-k}\right]_{\text{ads}}^{z_1-y}$ complex with chloride ions. It follows that aluminum in the presence of chloride ions undergoes a nucleophilic substitution reaction of the associative type [6, 7].

**Figure 2.** Effect of NaCl concentration on the aluminum LA process rate ($1/t_{\text{ind}}$), $t = 20^\circ\text{C}$.

Let us now turn to the analysis of the anodic behavior of aluminum in the presence of glycine at different pH values, which significantly affects the dissociative processes involving glycine in its most stable ionic form and the efficiency of organic compounds acting on passive aluminum. Experimental results obtained in aqueous glycine solutions (pH = 4.8–5.8) where the amino acid (AA) is present in the zwitter-ionic form [8] show that, according to electrochemical data (Figure 3), aluminum is in a passive state in these systems. This conclusion is confirmed by microscopic observations of the topography of the metal surface after recording the voltammograms (Table 1), which indicate the absence of local corrosion lesions on it. It is interesting to note that in the solutions studied, the rate of the anodic process at a fixed potential is almost independent of the concentration of the organic additive (Figure 4). This suggests that glycine zwitter-ions do not participate in the anodic process on aluminum, while the passivating layer, due to the high chemical affinity of Al for oxygen [9], is formed by interaction of the metal with water according to the scheme:



A possible reason of the observed effect may lie in the strong intermolecular hydrogen bonds that are formed between the amino and carboxy groups ($\text{NH}_3^+ \cdots ^-\text{OOC}$) of the AA zwitter form and prevail over the interaction of these groups with the oxidized surface of aluminum [8].

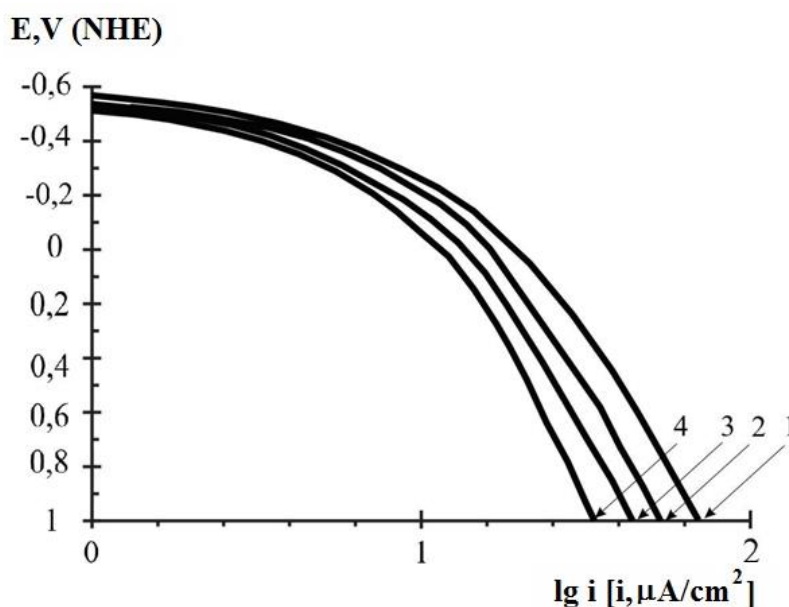


Figure 3. APC of aluminum in $1.3 \cdot 10^{-4}$ M (1), $1.3 \cdot 10^{-3}$ M (2), $1.3 \cdot 10^{-2}$ M (3), $1.3 \cdot 10^{-1}$ M (4) glycine solutions ($v = 0.2$ V/min, $t = 20^\circ\text{C}$)

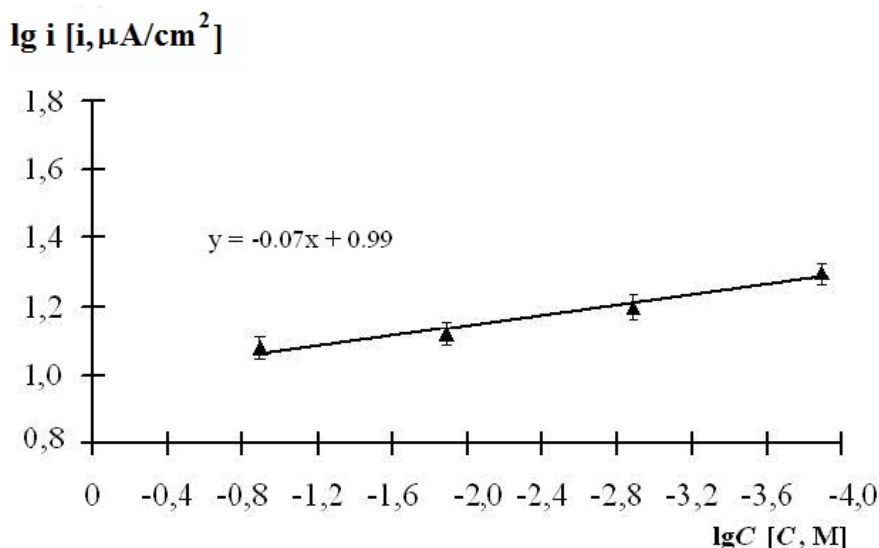
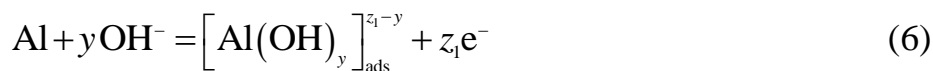


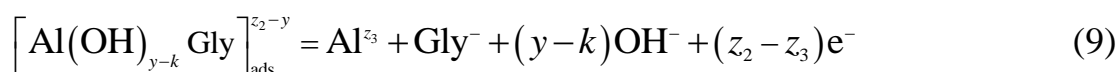
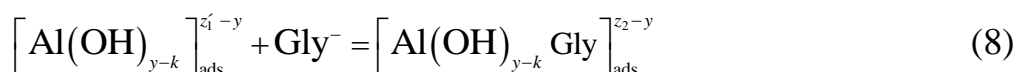
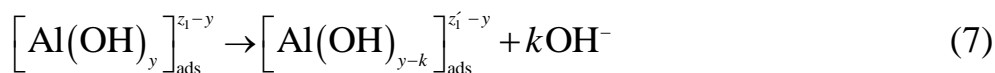
Figure 4. Effect of glycine concentration on the rate of the anodic process on aluminum at a potential of $E = 0.00$ V.

Since literature data on the high complexing and adsorption capacity of glycine are available [8, 10–14], it was of particular interest to analyze the anodic behavior of aluminum in systems where the AA being studied is present in anionic form. For this purpose, a series of experiments similar to those discussed above in slightly alkaline solutions with a fixed pH value of 8.5 and varying concentrations of glycine were carried out (Figure 5). Analysis of the data obtained showed that aluminum underwent PF in solutions with Gly^- in the entire concentration range studied from $1.3 \cdot 10^{-4}$ M to $1.3 \cdot 10^{-1}$ M. It should be noted that the diameter and depth of pits formed on aluminum in the presence of glycine are significantly smaller than in NaCl solutions ($h = 3\text{--}6$ μm , whereas this value was about 12 μm in the presence of chloride ions (Table 1)). However, in electrolytes with organic additives, the PF mechanism corresponds to the nucleophilic substitution model [2, 6, 7] and is similar to the above-described mechanism with chloride ions. Summarizing the experimental results and comparing them with the literature data allowed us to assume the following scheme of the stage of the aluminum PF mechanism, including:

- formation of a passivating film on the metal surface:



- PF process:



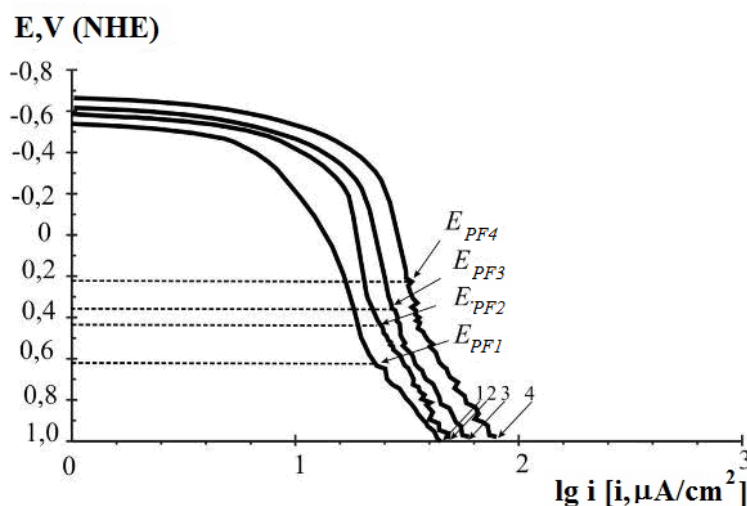


Figure 5. APC of aluminum in $1.3 \cdot 10^{-4}$ M (1), $1.3 \cdot 10^{-3}$ M (2), $1.3 \cdot 10^{-2}$ M (3), $1.3 \cdot 10^{-1}$ M (4) glycine solutions with pH 8.5 ($v = 0.2$ V/min, $t = 20^\circ\text{C}$).

The specificity of this system is that the surface complex $\left[\text{Al}(\text{OH})_{y-k}\text{Gly}\right]_{\text{ads}}^{z_2-y}$ is a compound – aluminum dihydroxoglycinate $\text{Al}(\text{OH})_2\text{Gly}$ [15], which is sufficiently soluble in the alkaline medium. This effect leads to a change in the stage controlling the PF process: in the latter case, its role is played by the dissociation of the starting $\left[\text{Al}(\text{OH})_y\right]_{\text{ads}}^{z_1-y}$ complex (7). The data obtained correlate with the results of formal kinetic analysis, according to which $n_{\text{Gly}^-} = d(\lg 1/t_{\text{ind}})/d\lg C_{\text{Gly}^-} \sim 0.2 \rightarrow 0$ (Figure 6), hence it follows that the PF on aluminum in the presence of Gly^- anions is a nucleophilic substitution reaction of dissociative type [6, 7].

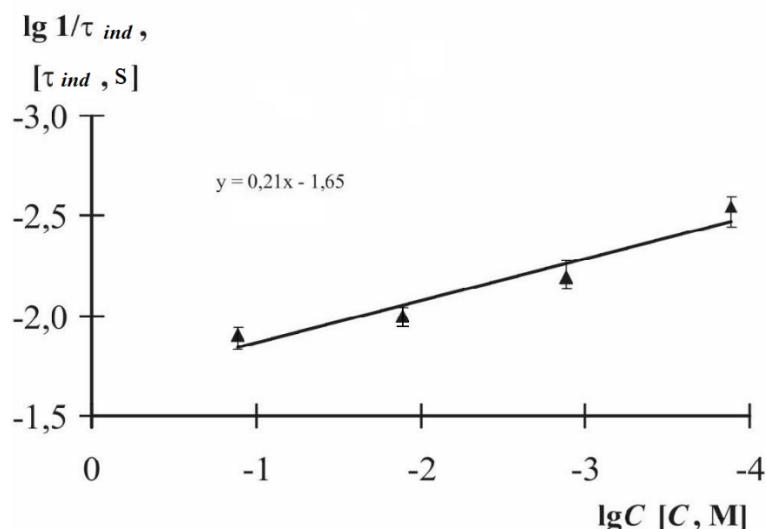


Figure 6. Effect of the concentration of glycinate ions on the aluminum LA process rate ($1/t_{\text{ind}}$), $t = 20^\circ\text{C}$.

Conclusions

1. Based on a set of physical and chemical studies, systematic data on the anodic behavior of aluminum in a series of aqueous solutions with inorganic (NaCl) and organic (glycine) additives at pH=4.8–8.5 have been obtained.
2. It has been shown that the zwitter ions of glycine have no noticeable effect on the anodic behavior of the metal, which is in a stable passive state at pH=4.8–5.8, that is, near the isoelectric point (pI=5.97). The observed effect may result from the strong intermolecular hydrogen bonds that exist between the amino and carboxy groups and prevail over the interaction of these groups with the oxidized aluminum surface.
3. The corrosive effect of Cl^- and Gly^- ions on aluminum, which causes its local activation at all NaCl (pH 4.8–5.8) and glycine (pH 8.5) concentrations studied (from $1.3 \cdot 10^{-4}$ M to $1.7 \cdot 10^{-1}$ M) has been proved.
4. Based on modern theories of competitive adsorption, complexation and nucleophilic substitution, assumptions have been made about the mechanisms of aluminum PF. They have been confirmed by independent physical and chemical methods (electrochemical and scanning electron microscopy combined with RSMA). The PF process is a nucleophilic substitution reaction of associative type in the presence of chloride ions, and of dissociative type in the presence of glycine anions.

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